GREEN SYNTHESIS OF NANOHYBRID COMPOSITES FOR DETOXIFICATION OF ENVIRONMENTALLY PERSISTENT POLLUTANTS

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CERTIFICATE

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TABLE OF CONTENTS

Sr.no	Chapter	Page no.
1	Introduction	1-5
2	Literature review	6-9
3	Research gap	10
4	Research objectives	11
5	Research Methodology	12-17
6	Significance	18
7	References	19-25

1. INTRODUCTION

The environment encompasses the surroundings where humans, plants, animals, and microorganisms exist or operate. It includes the land, Earth's atmosphere, and water. The Earth's system is characterized by four interconnected spheres: the biosphere (consisting of living organisms), the atmosphere (comprising air), the lithosphere (encompassing land), and the hydrosphere (including water). These spheres interact in harmony to sustain life on Earth. Environmental contaminants and pollutants are chemicals found in higher concentrations than natural levels in various parts of the environment (Masindi, V., *et al., 2018*, Beasley, V., *et al., 2012*, Martin, Y.E., *et al., 2012*). During the last hundred years, industrialisation has grown at a fast rate. It has thus increased the demand for exploitation of the Earth's natural resources at a careless rate, which has exacerbated the world's problem of environmental pollution (Gautam, P.K., *et al., 2016*). The environment has suffered severe pollution from various sources including inorganic ions, organic pollutants, organometallic compounds, radioactive isotopes, gaseous pollutants, and nanoparticles (Beasley, V., *et al., 2012*).There has been an ongoing discussion with regards to the definition of the term 'heavy metals'.

Heavy metals are defined either by their high atomic weight or density. In contemporary usage, the term "heavy metal" refers to metallic chemical elements and metalloids that are toxic to both the environment and humans. While some metalloids and lighter metals like selenium, arsenic, and aluminum are toxic and classified as heavy metals, certain heavy metals like gold are typically non-toxic (Briffa, J., *et al., 2020,*Duffus, J.H., *et al., 2001*,Wang, L.K., *et al., 2009*). Heavy metals are naturally occurring elements present in the Earth's crust since its formation. However, the significant rise in their use has led to a dramatic increase in metallic substances in both terrestrial and aquatic environments (Gautam, P.K., *et al.2016*).

Some heavy metals serve as essential components necessary for metabolic activities in living beings, albeit in small amounts (Raval, N.P., *et al., 2016*). However, in larger quantities, these same metals can cause irreversible toxicity to human health (Koedrith, P., *et al., 2013*). Heavy metals discharged into open waters have devastating effects on aquatic life, including oxygen depletion and algal blooms. Upon entering rivers, these metals convert into highly toxic hydrated ions, disrupting enzymatic processes and exhibiting faster absorption rates. Removing heavy metals is essential to reduce public health risks. Despite regulations set by organizations like the World Health Organization (WHO) and the Environmental Protection Agency (EPA)to

limit heavy metal discharge, effluents often exceed permissible levels, leading to human health and environmental issues. Some toxic heavy metals include Lead, nickel, arsenic, chromium, zinc, copper, cadmium, cobalt, antimony, etc.

Heavy metal ions can cause many adverse effects like cancer, kidney damage, hepatitis, miscarriages, anemia, encephalopathy, and nephritic syndrome (Sardans, J., *et al.,2011*). Lead ions are commonly released into the environment from various sources such as metal mining industries, acid lead battery manufacturing, paper production, glass manufacturing, and polishing industries. On the other hand, cadmium is often found in water discharged from electroplating operations, the production of batteries, photovoltaic cells, metallurgical processes, and fabric factories (Wang, X., *et al., 2012*). Nickel ions, commonly found in jewelry, zips, watches, and coins, can lead to skin diseases upon contact, including allergic reactions and dermatitis. Chromium metal ions, specifically in the hexavalent (VI) state, are associated with severe health issues such as liver damage, nephritis, and stomach distress. Additionally, Cr (VI) ions are a major contributor to the development of nasal mucous ulcers. These health risks underscore the importance of minimizing exposure to these toxic compounds to protect human health (Moreno-Castilla, C., *et al., 2004*).

The adsorption of heavy metal ions onto carbon nanomaterials is an effective method for mitigating heavy metal contamination in the environment. Various sources contribute to this contamination, underlining the urgency of addressing it due to its severe adverse health effects. Removal of heavy metal ions from water is crucial for safeguarding human lives. Several methods can achieve this, including ion exchange, reverse osmosis, precipitation filtration, biosorption, coagulation, and extraction. Each method offers unique advantages and applications, emphasizing the importance of employing diverse strategies to combat heavy metal pollution and protect public health (Fu, F., *et al., 2011*, Huang, Q., *et al.,2018*). Adsorption is widely regarded as the best method for removing trace levels of heavy metal ions due to its cost-effectiveness, high efficiency, and ease of operation (Czikkely, M., *et al., 2018*). Various materials, including plant adsorbents and organic substances like humic acid, have been utilized for water treatment purposes. Humic acid, in particular, has found widespread application in water disinfection and the removal of heavy metal ions (Hankins, N.P., *et al., 2006*, Parvin, A., *et al., 2016*, Baby, R., *et al., 2019*, Huang, Q., *et al., 2018*). (Tang, W.W., *et al., 2014*). Nanotechnology platforms are extensively applied across various fields, including environmental science, health sciences, electronics, industrial separation, portable water

treatment in both large and small-scale plants, catalyst development, and energy storage andgeneration (Zeng, G., *et al., 2018*, Zeng, Meiying Liu., *et al., 2016*, Liu,Y., *et al., 2018*).

Nanomaterials offer a unique platform for purifying contaminated water due to their high surface area, chemical modification capabilities, and ease of regeneration. Increasingly, nanomaterials are being utilized for removing various pollutants, including organics, metal ions, biological contaminants, and arsenic, from watersources (Al-Senani,G.M., *et al., 2018,* Bpozbas, S.K., *et al., 2016,* Brunet, L., *et al., 2009*, Appenroth, K.J., *et al., 2010*).

Latest advancements in the application of carbon nanomaterials, including graphene, graphene oxide, carbon nanotubes (CNTs), fullerenes, and activated carbons, for purifying heavy metal ion-contaminated water. These carbon nanomaterials are known for their exceptional chemical, mechanical, thermal, and electrical characteristics, making them versatile tools in various fields such as energy storage, sensors, electronics, drug delivery, and disease diagnosis. The focus of this review is on their use specifically in the purification of water contaminated with heavy metal ions.

Metal oxide nanoparticles (MO-NPs) smaller than 100 nm are extensively utilized in nanoscience, particularly in nanoscience, which holds significant promise for applications in biological science and pharmaceutical technology. In recent years, there has been a notable focus on MO-NPs due to their exceptional properties and diverse applications. Synthesis methods for MO-NPs have garnered considerable attention in nanotechnology research, driven by rising demand across industries and medical sectors. These nanoparticles find utility in various applications such as fillers, disinfectants, optics, antimicrobial agents, drug delivery systems, and catalytic products (Muthuvel, A., *et al., 2020*). Metal oxide nanoparticles (MO-NPs), including CuO, CaO, TiO_2, and ZnO, have been extensively studied for their environmental and biomedical applications. Among them, cerium oxide nanoparticles (CeO_2-NPs) have attracted significant attention from researchers due to their versatile applications. These include catalysis, water purification through photocatalysis, utilization in batteries, and as anti-microbial agents (Rajeshkumar, S., *et al., 2018*). CeO_2-NPs exhibit superoxide-dismutase-like activity, offering inhibition against cardiac myopathy and providing protection from radiation to normal cells (Jing, C., *et al., 2019*).

Various methods are utilized for the synthesis of nanoparticles (NPs) through chemical routes, including co-precipitation methods, solvothermal synthesis, template-assisted precipitation, spray drying system, sonochemical methods, hydrothermal synthesis, and sol-gel method etc.,

Compared to other methods, chemical synthesis of nanoparticles is considered easy, cost-effective, and environmentally friendly, as it reduces the use of toxic substances that can impact human health and the environment. There is a growing demand for developing safe, simple, and eco-friendly methods for synthesizing nanoparticles. Biosynthesis of nanoparticles has been achieved using various microorganisms such as fungi, yeast, bacteria, and enzymes. Additionally, nanoparticles synthesized from plant extracts are deemed safe to handle, readily available, and offer a wide range of metabolites. Phytochemicals like carbohydrates, saponins, amino acids, flavonoids, terpenoids, and proteins present in plant extracts play a crucial role in the synthesis of nanoparticles (Muthuvel, A., *et al., 2020*). Biochar, also known as pyrogenic black carbon, is a carbon-rich, porous substance created through the thermal degradation of biomass via pyrolysis in oxygen-deficient conditions (Vijayaraghavan, K., *et al., 2018*).

Biochar has garnered significant attention recently due to its distinctive features, such as its potential for carbon sequestration, production of bioenergy, enhancement of soil fertility (Inyang, M.I., *et al., 2016*) and its crucial role in environmental remediation (**Figure 1**). The carbon-rich composition, high porosity, and extensive surface area of biochar play a crucial role in the sorption of toxic heavy metals from contaminated water (Qambrani, N.A., *et al., 2017*). Moreover, the presence of various functional groups on the surface of biochar, such as hydroxyl, carboxyl, alkyl, phenolic, and amino groups, enhances its affinity for sorbing metals from contaminated water. This attraction extends to a range of heavy metals including nickel (Ni), cobalt (Co), mercury (Hg), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), and lead (Pb) (Ahmed, M., *et al., 2014*, Cheng, Q., *et al., 2016*). Biochar can be produced through various processes, including slow or fast pyrolysis, gasification, and combustion (Zhou, Z., *et al., 2017*).

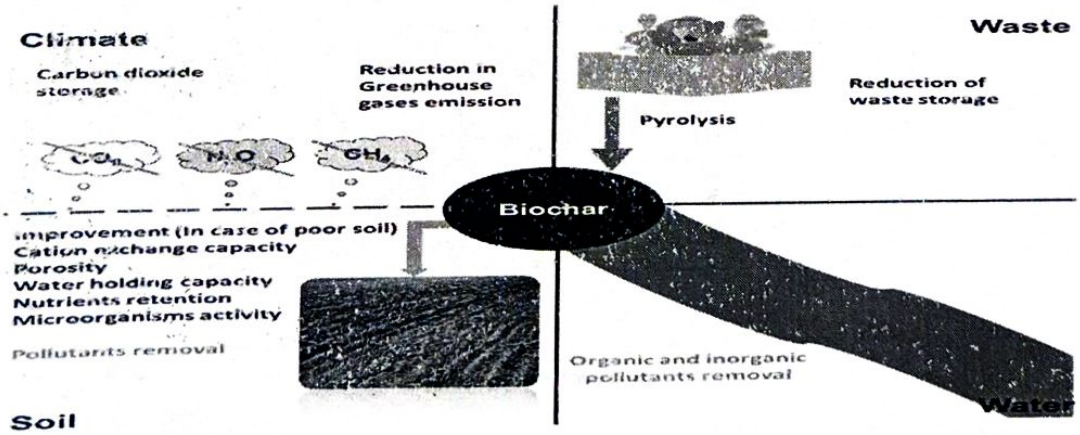


Figure 1. Importance of biochar in various compartments of the environment.

A variety of organic wastes and materials have been utilized to produce biochar, including raw pine chips, paper-mill waste, plant tissue, peanut hulls, pecan shells, pine chips, poultry litters, forage plant biomass, citrus wood, empty fruit bunches, cotton seed hulls, rubber wood sawdust, sewage bio solids, rice husks, poultry manure, human manure, swine manure, goat manure, and agro-industrial biomass. The properties and quality of the biochar, as well as its potential for use in remediating contaminated water, are strongly influenced by the type of biomass materials and pyrolysis conditions (Lee, H.W., *et al., 2018*).

Compared to activated carbon, biochar serves as an excellent sorbent material, offering advantages such as low cost, easy availability, and a high affinity for removing heavy metals from contaminated aqueous media (Liu, Z., *et al., 2010*). Biochar has demonstrated heavy metal sorption capacities ranging from 19.2 to 33.4 mg/g for Ni, 2.4 to 147 mg/g for Pb, 3 to 123 mg/g for Cr, and 0.3 to 39.1 mg/g for Cd, as reported by (Inyang, *et al.,2016*). However, these capacities are lower compared to modified or activated biochar, which exhibit higher sorption capacities of 255 mg/g for Pb and 91.4 mg/g for Cd (Wilsom, K., *et al., 2006*). Hence, the sorption capacity of biochars has been significantly enhanced through methods such as loading the biochar with various organic functional groups, minerals, nanoparticles, reductants, as well as activation with acid or alkali solutions (Zhou, Y., *et al., 2014*).

2. LITERATURE REVIEW

Wastewater, a byproduct of municipal activities, harbors a medley of contaminants including organic substances, microorganisms, inorganic compounds, and toxic heavy metals. These impurities alter the chemical, biological, and physical attributes of clean water, posing significant environmental and health risks if not properly treated (Abou El-Nour, K.M., *et al., 2010*). Effluent treatment relies on three fundamental principles: physical treatment, chemical treatment, and biological treatment. Physical treatment utilizes processes like adsorption and radiation. Adsorbents like activated charcoal, zeolite, chitosan, and industrial wastes are commonly employed in water treatment plants for adsorption (Maleki, A., *et al., 2015*). Municipal wastewater undergoes radiation treatment using UV, gamma, and X-rays (Taghipour, F., *et al., 2004*). Chemical treatment employs oxidation and reduction techniques utilizing various chemical compounds. Biological treatment is favored for its specificity compared to other methods.

Nanoparticles, ranging from 1 to 100 nm in size, exhibit unique characteristics not found in bulk materials. Their significance lies in the high surface area available for chemical reactivity, a feature absents in bulk forms (Stoimenov, P.K., *et al., 2002*). Four classes of functional nanoparticles are utilized in water purification: dendrimers, metal-containing nanoparticles, zeolites, and carbonaceous nanomaterials (Savage, N., *et al., 2005*). The nanomaterials listed in Table1 are effective for removing various dyes and contaminants from water. Micro and Nano fillers typically require higher working pressures to retain solutes with molecular masses between 1000 and 3000 Da. This challenge has been addressed by dendrimer ultrafilters (Savage, N., *et al., 2005*). Metal-containing nanoparticles serve as efficient biocides, capable of eliminating bacteria from both gram-positive and gram-negative groups. Additionally, they facilitate the removal of heavy metals like arsenic and halogens (Sudha, A., *et al., 2017*). Zeolites serve as an ion exchange medium, effectively removing heavy metals from water (Nichols, W.T., *et al., 2006*). Carbonaceous materials can act as sorbents for organic solutes in aqueous environments. A recent advancement involves the utilization of biogenic nanoparticle-incorporated membranes for the degradation of toxic chlorinated compounds (Smuleac, V., *et al., 2011*). Membranes functionalized with biologically synthesized nanoparticles and immobilized enzymes demonstrate superior performance in enzyme reactions compared to single-phase reactions, with enhanced nanoparticle (Virkutyte, J., *et al., 2011*). Stacking membranes with different immobilized enzymes enables catalysis at a faster rate.

Metallic nanoparticles are synthesized using both destructive and constructive methods, utilizing metal precursors to create pure nanoparticles. These nanoparticles exhibit unique opt electrical properties due to plasma resonance characteristics. Synthesis is controlled by factors like shape, facet, and size (Drdem, E.C., *et al., 2012)*. All metals can be synthesized into nanoparticles, with aluminum, gold, iron, lead, silver, cobalt, zinc, cadmium, and copper being well-known examples. Nanoparticles, typically ranging from 10 to 100 nm in size, display distinctive properties influenced by surface characteristics, structure, shape, color, and environmental factors like sunlight, moisture, air, and heat.

Investigate on Heavy metal removal from wastewater using low cost adsorbents. With the onset of industrialization mankind has witnessed various environmental issues in the society. The conventional methods of treatments of heavy metal contamination includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electro dialysis etc. These methods are costly, energy intensive and often associated eith gemeration of toxic byproducts. Thus, the absorption has been investigated as a cost effective methods of removal of heavy metals from water waste. In the present study various low cost adsorbent has been reviewed as an abatement of heavy metal pollution from water waste.

These adsorbents include materials of natural origin like zeolites, clay, peat, moss and chitin found to be effective agent for removal of toxic heavy metals like Pd, Cd, Zn, Ni, Ag, Hg, Cr etc. Apart from these various agricultural wastes like rice husk, neem bark, black gram, waste tea, Turkish coffee, walnut shell etc. were also established as a potent adsorbent for heavy metal removal. Beside that low cost industrial by products like fly ash, blast furnace sludge, waste slurry, ligin, iron hydroxide, and red mud, coffee husks, Areca waste, tea factory waste, sugar beet pulp, battery industry waste, sea nodule residue and grape stalk wastes have been explored for their technical feasibility to remove toxic heavy metals from contaminated water (**Table 1**) (Amuda, O.S., *et al., 2006*).

Some previous studies have shown that the carbon based materials can be used in the fabrication of heterojunctions which not only provide support to the photocatalysts but also overcome the complication related to agglomeration, surface area, and stability (Chen, J.P., *et al., 2003*). Biochar is a carbonaceous material which is produced by the pyrolysis of biomass in oxygen limited environment under the N_2 atmosphere. When biochar or carbon based materials such as RGO, GO, activated carbon are used in the fabrication of composites, these

may act as co-catalysts to provide sufficient catalytic sites for photocatalytic degradation (Liao, G., *et al., 2012*).

Recently various researchers have evaluated the potential of biochar in the solar light driven photocatalysis and it is observed that carbon materials can act as co-catalysts to provide sufficient catalytic sites for photocatalytic degradation and can also act as competent electron transfer channel as well acceptor which effectively decrease the charge recombination rate. Yan et al and co-worker have found that biochar has the strong response in UV light (Wu, j., *et al., 2017*). Some research group have demonstrated that biochar has potential to generate reactive oxygen species such as •OH, $•O_2$-, H_2O_2 even in the absence of a semiconductor when subjected to UV light illumination (Matos, J., *et al., 2016*). Thus biochar is supposed to active material replacing the conventional material which are used as supports due to their high coast and complex synthesis such as bentonite, glass, silica etc.

Semiconductor nanocomposites have been investigated as an efficient phtocatalysts for the degradation of toxic contaminants. TiO_2 is the most popular and extensively used photocatalyst for water purification due to high reactivity, stability against photo-corrosion, non-toxic nature and insoluble in water under ambient conditions. Titanium dioxide has greater surface area and difficult to recover the TiO_2 from aqueous system. Therefore, some investigators encapsulated the TiO_2 into the various support materials such as glass fibers, quartz and stainless steel (Yu, H., *et al., 2006*). Although, these investigations offer the facile way to overcome the separation problem. However, photocatalytic efficiency of nanocomposites dropped to a considerable extent due to reduction in surface area and mass-transfer rate after amalgamation process.

In a photocatalytic process adsorption play an important role in the mineralization of a target pollutant. Because the interaction of pollutant molecule with a photocatalysts is a prerequisite step. Thus adsorption provide better chance of interaction to a photocatalysts with pollutant in a photodegradation process. Many researchers have studied the synergism of adsorption and photocatalysis (removal of malachite green and methylene blue) (Kumar, S., *et al., 2013*) and (photocatalyst activity toward Congo red) (Lan, S., *et al., 2014*).

Many research groups have worked on removal of paraben from wastewater as well in simulated waste water photocatalytic degradation of benzyl paraben by TiO_2, photosensitized oxidation of mixture of parabens in aqueous solution Photodegradation of parabens by Fe(III)-

citrate complexes (Feng, X., *et al., 2014*), methyl paraben removal using heterogeneous photocatalysis (Zuniga-Benitez, H., *et al., 2017*) and adsorption of Methyl paraben by sub micro-sized molecularly imprinted polymer.

Thus various research community have worked on the decontamination of water from such persistent pollutants e.g. degradation of the 2,4-D by ozonation catalyzed with Fe^{2+} and UVA light (Brillas, E., *et al., 2003*), sonolysis of 2,4-D (Peller, J., *et al., 2001*), degradation of 2,4-D by electro-oxidation and Electro-Fenton/BDD Processes, efficient degradation of 2,4-D by peroxymonosulfate/ magnetic copper ferrite nanoparticles/ozone (Jaafrarzadeh, N., *et al., 2017*) photocatalytic degradation of paraquat dichloride over CeO_2-modified TiO_2 nanotubes,TiO_2 nanotube arrays for photocatalytic degradation of paraquat (Marien, C.B., *et al., 2016*), degradation of paraquat by heterojunction $ZrTiO_4/ZrTi_2O_6/TiO_2$ photocatalytic degradation of paraquat using nano-sized Cu-TiO_2/SBA-15 under UV and visible light (Sorolla II, M.G., *et al., 2012*).

Table 1: Types of nanomaterials used in the removal of contaminants present in wastewater.

Functional nanoparticle category	**Contaminant(s) targeted**
Dendrimers (a core, interior branch cells and terminal branch cell)	Dissolved organic, inorganic solutes (molecular mass less than 1000 Da) and certain classes of microbes
Metal nanoparticles (Mg, Ag, Pt, Pa, Au, Fe, Co)	Halogen, tri-chloroethane, arsenic, heavy metals, and certain classes of microbes
Zeolite	Heavy metals like Cr, Zn, Ni, Cu, Cd
Carbonaceous nanoparticles	Organic solutes and microorganisms

3. RESEARCH GAP

Recent advancements in wastewater treatment have seen significant progress, particularly through the application of advanced materials such as nanomaterials and modified adsorbents. These materials have demonstrated enhanced capabilities in removing a wide array of pollutants due to their high surface areas and reactivity. However, despite these advancements, there remains a crucial need to develop new, sustainable, and cost-effective adsorbent materials with improved adsorption capacities and selectivity to address a broader range of pollutants. Bringing these knowledge gaps is essential for the effective integration of adsorption technology into existing wastewater treatment systems. Addressing the challenges related to reactor design, flow dynamics, and mass transfer limitations will maximize the potential of adsorption methods for sustainable and cost-effective pollutant removal on a broader scale.

4. RESEARCH OBJECTIVES

Based upon the aforementioned discussion, the following objectives have been planned for current research work:

1. To prepare the activated biochar from agro-waste materials namely: *Pinus (needle), Cassia fistula (peels),* and *Achyranthes apsera (stem).*
2. To synthesize the biochar-supported Al_2O_3-CeO_2 (Aluminium oxide- Cerium oxide) composites using *Hibicus rosa* leaf extract.
3. To promote the green synthesis of biochar-supported Al-Mo (Aluminium-Molybdenum) and Ce-Mo(Cerium-Molybdenum) doped copper oxide composites using the co-precipitation technique.
4. To characterize the prepared sample with various characterization techniques such as field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), XPS, BET, Fourier transform infrared microscopy (FTIR), X-ray diffraction (XRD), energy Dispersive X-ray (EDX) and UV- visible spectra, etc.
5. To study the adsorption and photocatalytic remediation of emerging pollutants from industrial effluents using prepared biochar/nano-composites.

5. RESEARCH METHODOLOGY

5.1. Chemical Required

Chemicals required such as Hydrochloric acid (HCL), Ethanol (C_2H_5O), Cupric Sulphate ($CuSo_4$), Ammonium Molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$], Sodium Hydroxide (NaOH), Sodium Borohydride ($NaBH_4$), Polyvinylpyrrolidine(PVP) $(C_6H_9NO)_n$, Aluminum Nitrate $[Al(No_3)]_3$, Ammonium ceric nitrate purchased from Hebansh Pharma Equipments Himachal Pradesh, India.

5.2. Synthesis of Leaf extract

Hibiscus rosa plant leaves were collected from the forest i.e. Hamirpur, Himachal Pradesh, India. The leaves were washed several times with distilled water to remove all dust particles or impurities and then dried in sunlight. Grind all leaves to make a fine powder. The 10 g of washed, dried, fine powder leaves were in a 250 ml glass beaker and 100 ml of distilled water. The mixture was boiled for 60 min until the colour of the solution changed from watery to light yellow by using a magnetic stirrer. The extract was cooled to room temperature, and filtered using filter paper. The extract was stored in a refrigerator to be used for further experiments.

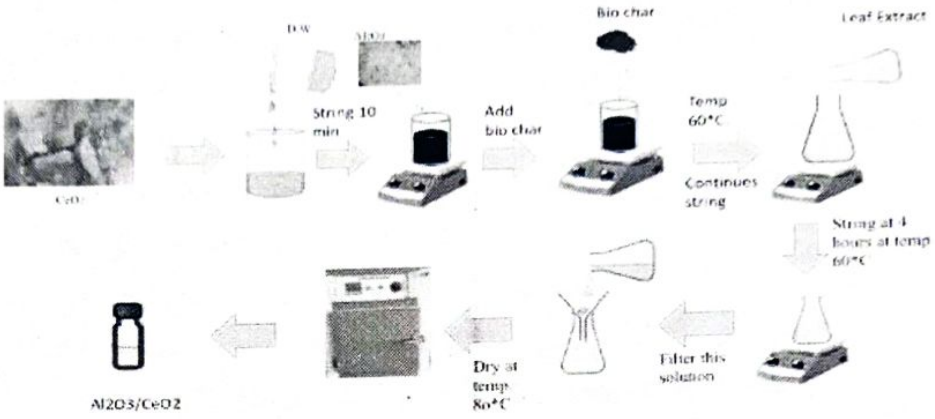
5.3. Synthesis of Biochar

Plants-based materials of *Pine needles, Cassia fistula,* and *Achyranthes apsera* were obtained from the forest i.e. Hamirpur, Himachal Pradesh, India. The selected materials have been washed with distilled water to remove all impurities and contaminants. Then, after it was completed dried and slashed into small pieces. Then all selected materials were grinded in fine powder forms. After this about 10 gm of fine powder of pine needle in a crucible was pyrolyzed in a muffle furnace at 180 ^{0}C for 2-3 hours. The crucible was allowed to cool down to room temperature and stored obtained materials in glass vials. The same procedure was followed for the formation of *Cassia fistula* and *Achyranthes apsera* biochar.

5.4. Green Synthesis of Al_2O_3/CeO_2/Biochar

50 ml of double-dissolved water was used to dissolve 0.375 g of aluminium oxide in a 250 ml beaker, and 50 ml of double-distilled water was used to dissolve 0.434 g of cerium oxide in a separate 250 ml beaker. Stirring both solution 10 min and after this mixed both solution in 500 ml of beaker. Add 0.1 g of biochar in above solution and stirring for 10 minutes and 5 ml of leaf extract put in above solution. After mixing all above in solution heat 60 ^{0}C and stirring for 4 hour's. After 4 hour's filter this solution wash with several time with distilled water for remove impurity. After filtration

collected nanocomposite dry it for 12 hours at oven at temperature 80 ^{0}C and store it dry glass vile. **Scheme 1** represent diagrammatic structure of green Synthesis of Al_2O_3/CeO_2/Biochar.



Scheme 1: Green synthesis of biochar/Al_2O_3/CeO_2 nanocomposite.

5.5. Characterization Techniques

5.5.1. Fourier transform infrared (FTIR) analysis

Fourier transform infrared spectroscopy is a powerful analytical technique that provides sufficient information about the structure of organic compounds. It helps in the identification of unknown compounds and determines the quality of a sample and the quantity of components present in the mixture. This technique is based on the principle that when IR radiation is passed through a sample, some radiations are absorbed or transmitted by the sample. Radiations absorbed by the sample caused the excitation of molecules from lower to higher vibrational levels. All bonds present in the molecules are not capable of absorbing the IR radiations.

5.5.2. X-ray diffraction (XRD) pattern

X-ray diffraction (PXRD) pattern is a powerful, non-destructive and rapid technique. It is widely used for the identification of crystal structure of an unknown material and determination of sample purity. The analyzed material is commonly present in the powder form or finely grounded. This technique is also useful for the liquid suspension or polycrystalline solid.

5.5.3. Field emission scanning electron microscope (FESEM)

FESEM instrument is widely used for determining the morphological anatomy of an object. Field emission scanning electron microscope (FESEM) scan the

surface of an object with a high energy beam of electrons. These electrons interact with atoms to produce the signals. These signals contain necessary information such as topographical, chemical compositions, and electrical conductivity. The accelerated electrons in FESEM possess significant amounts of kinetic energy. The energy is dissipated as a variety of signals. These signals contain secondary and backscattered electrons that produce microscopic FESEM images or are used for surface imaging.

5.5.4. High-resolution transmission electron microscope (HRTEM)

A high-resolution transmission electron microscope (HRTEM) is an important tool that provides the necessary information such as crystal structure, internal morphology, compositions, particle size, etc. HRTEM images were captured on an FP5022/22-Tecnai G2 20S-TWIN (USA) transmission electron microscope at an acceleration voltage of 200 kV.

5.5.5. Energy dispersive X-ray (EDX)

Energy dispersive X-ray spectroscopy (EDX) is another powerful non-destructive technique used to determine the elemental compositions. EDX is furnished with either FESEM or HRTEM instruments. The electron beam excites the atoms in the sample and consequently, produces the X-rays to discharge the excess energy. EDX spectra are recorded from a particular point on the sample. Alternatively, an electron beam sweeps over a selected area of a sample to identify the presence of elements.

5.6. Photocatalytic degradation

The photocatalytic degradation of biosynthesized NPs was evaluated by the pollutant degradation under sunlight irradiation. Then 1.0 mg of photocatalyst was added in 100 mL (1×10^{-5} M) of pollutant aqueous solution was stirred in the dark condition for 10 min until equilibrium condition attains followed by continuous stirring. Afterwards, suspension was kept under sunlight and readings were taken for each 10 min up to 50 min. The suspension was changed from X colour to colourless. The final solution was analysed by using UV-vis spectrophotometer. The percentage of pollutant absorbed on the catalyst surface was calculated by following equation:

$$\text{Photocatalytic degradation}(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

where A_0 is initial in absorption and At is absorption after time t.

5.7. Adsorption Experiment

The removal mechanism of organic pollutant ions has been investigated using batch adsorption experiments. In this experiment, a certain amount of nanocomposite was immersed in the pollutant solution. The aqueous 100 ml solution of the pollutant was prepared in the 250 ml of Erlenmeyer flasks. The resulting solution was stirred on a thermal shaker for definite contact time. The pH of pollutant ions has been adjusted by adding a few drops of 0.1N HNO_3 or 0.1N NaOH. At the predetermined time, flasks were withdrawn from the thermal shaker. The solution was centrifuged at 7500 rpm for 20 min to eliminate the nanocomposite particles from an aqueous phase. Finally, samples were filtered using Whatman filter paper. After this, the filtrate was examined for residual pollutant concentration under a UV-visible spectrophotometer. The filtrate was analyzed at λ_{max} of X nm. The effect of various parameters such as initial pollutant concentrations (100-500 mg/L), nahocomposite dosage (20-80 mg/L), contact time (10-50 min), pH (2.0-14.0), and temperature (30-70 °C) have been studied and optimized. The adsorption capacity q_e (mg/g) was calculated by the following equation:

$$q_e = (C_i - Ce)\frac{V}{M} \tag{2}$$

Where, C_i and Ce indicate initial and equilibrium concentrations (mg/L), respectively. q_e (mg/g) expresses equilibrium adsorption capacity, V corresponds to volume of solution (ml) and M is the mass of nanocomposites (mg/L). The percentage adsorption of pollutants was calculated as:

$$\%\ \text{Removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{3}$$

C_i and C_e (mg/L) are initial and final pollutant concentrations before and after adsorption

5.8.Adsorption isotherms

In this study, the experimental data were interpreted using three prominent models: Langmuir, Freundlich, and Tempkin isotherms.

5.8.1. Langmuir isotherm

The Langmuir isotherm is expressed by the following equation:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{4}$$

where q_e is the amount of adsorbate adsorbed at equilibrium in mg g^{-1}, q_m is the maximum monolayer adsorption capacity of the adsorbent in mg g−1, C_e is the concentration of the adsorbate under equilibrium conditions in mg L^{-1} and K_L is the Langmuir constant in L mg^{-1}. The Langmuir isotherm can also be expressed in the following equation to determine the constants K_L and q_m:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L\, q_m C_e} \tag{5}$$

The values of the constants can be found from the intercept and slope of the linear plots of the experimental data of $(1/q_e)$ versus $(1/C_e)$ for the different pollutants.

5.8.2. Freundlich isotherms

The Freundlich isotherm is expressed by the following equation:

$$q_e = K_F\, C_e^{\frac{1}{n}} \tag{6}$$

where K_F and n are Freundlich constants. K_F is the adsorption capacity of the adsorbent in mg g^{-1} (L mg^{-1}), n and it represents the amount of adsorbate adsorbed onto the adsorbent for a unit equilibrium concentration. The values of the constants can be determined from the intercept and slope of the linear plots of the experimental data of $(\ln q_e)$ versus $(\ln C_e)$ for the different dyes and metal ions, following the equation below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

5.8.3. Tempkin isotherms

Tempkin and Pyzhev isotherm model may be presented by the following equation:

$$q_e = \frac{RT}{b}\, ln(K_F\, C_e) \tag{8}$$

Linearized Tempkin isotherm equation can be written as follows:

$$q_e = B_i \ln(K_T) + B_i \ln (C_e) \tag{9}$$

$$B_i = \frac{R_T}{b} \tag{10}$$

Where, T is the absolute temperature (K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and a fitting plot between q_e and ln C_e determines the values of B_i and K_T, which were computed from the slope and intercept, respectively.

5.9. Kinetic study

Adsorption is a time dependent mechanism and inspected in terms of many processes such as diffusion model and chemical reaction. The linear equation for pseudo-first-order can be written as:

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303} \times t \quad (11)$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively.

5.10. Thermodynamic study

The nature of the adsorption process will be explained in terms of thermodynamic parameters such as Gibbs free energy (ΔG^O), enthalpy (ΔH^O), and change in entropy (ΔS^O). The equation for thermodynamics can be represented as:

$$\Delta G^0 = \Delta H^0 - \Delta S^0 \quad (12)$$

To investigate whether the adsorption is spontaneous and explore the mechanism involved in the adsorption process the thermodynamic parameters can be determined by following equations:

$$\Delta G = -R_T \ln K_d \quad (13)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{R_T} \quad (14)$$

where, ΔS (J $mol^{-1}k^{-1}$), ΔH (k_J mol^{-1}), and ΔG (k_J mol^{-1}) are the entropy change, enthalpy change, and Gibbs free energy change respectively. R (8.314 J mol^{-1} k^{-1}) is the gas constant and T (K) is the temperature.

6. SIGNIFICANCE

The removal of pollutants by adsorption and Photodegradation technique lies in its effectiveness in improving water quality and mitigating environmental pollution. Removal of heavy metals ions and dissolved organic compounds present in wastewater is a challenge for many countries owing to high cost of existing technologies and continued increase in water consumption. In three natural materials, *Pine needle, Cassia fistula (peels)* and *Achyranthes apsera(steam)* were selected and used as simple and renewable adsorbents for water purification. This not only benefits the wastewater treatment but also reduce the release of harmful pollutants into natural eco-system, safeguarding the human health and environment system. By conducting research in this field, we can optimize the adsorbent materials, modify operating conditions or develop novel techniques. Traditional methods of pollutant removal, such as chemical treatments or physical adsorption, often have limitations in terms of efficiency, cost, and environmental impact. Nanocomposites offer a promising alternative, capable of degrading organic pollutants through advanced mechanisms such as catalytic reactions or photocatalysis. By combining these nanocomposites with biochar, the research Sneed for harmful chemicals and minimizing waste generation.

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COMMENTS FROM EXTERNAL EXPERT

The following suggestion has been given by an external subject expert:

1. **Comment** – The title needs to be changed.

   Response – The title has been changed as suggested (Green Synthesis of Nanohybrid Composites for Detoxification of Environmentally Persistent Pollutants).

2. **Comment** – The plant's botanical name should be italicized with the first letter in uppercase.

   Response – This has been changed according to an external expert.

3. **Comment** – Use ml instead of mL, g for gram, min rather than minutes.

   Response – All necessary changes has been done.